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 - a. Rejection of Stochastic Noise in low-level light pulsed light scattering experiments, Jyhpyng Wang and Eric Mazur, Rev. Sci. Instrum., 64 (1993) 2550
 - b. Coherent anti-Stokes Raman spectroscopy of infrared multiphoton excited molecules, S. Deliwala, J. Goldman, K-H. Chen, C-Z Lü, E. Mazur, J. Chem. Phys. 101, 8517 (1994)
 - c. Subpicosecond laser-induced initiation of surface reactions: O₂ and CO on Pt(111), S. Deliwala, R.J. Finlay, J.R. Goldman, T.H. Her, W.D. Mieher, and E. Mazur, Chem. Phys. Lett., accepted for publication
 - d. Femtosecond laser activation of surface reactions, R.J. Finlay, S. Deliwala, T.-H. Her, J.R. Goldman, W.D. Mieher, C. Wu, and E. Mazur in *Laser Techniques for Surface Science II*, SPIE Proceedings, 2547 (1995).
8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

Prof. Eric Mazur	—	half period (summers)
Dr. Walter Mieher	—	half period
Mr. S. Deliwala	—	half period
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Mr. Aryeh Feder	—	AASERT Fall 94

Mr. J. Goldman was awarded the Ph.D. degree in July 1994 on a thesis entitled "Laser studies of energy- and charge-transfer dynamics".

Mr. S. Deliwala obtained the Ph.D. degree in March 1995 on a thesis entitled "Time-resolved studies of molecular dynamics using nano- and femto-second laser pulses".

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13. ABSTRACT (Maximum 200 words) The thrust of this project was to perform ultrafast time-resolved spectroscopy of surface adsorbed molecules and reaction processes. The two major objectives were: 1) to combine new ultrafast optical probes with standard surface science probes by building a novel mode-locked, regeneratively amplified femtosecond Ti:sapphire laser facility and an ultrahigh vacuum surface science chamber, and 2) to study energy transfer and surface reactions in adsorbate/substrate systems. Both of these objectives were met. With the funds allocated under this contract we have <i>a</i>) developed a femtosecond, regeneratively-amplified Ti:Sapphire laser system, <i>b</i>) built a UHV surface science chamber, and <i>c</i>) performed novel measurements of the oxidation of CO and the desorption of O ₂ on a Pt(111) surface at 90 K.				
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BRIEF OUTLINE OF RESEARCH FINDINGS

1. The thrust of this project was to perform ultrafast time-resolved spectroscopy of surface adsorbed molecules and reaction processes. The two major objectives were: 1) to combine new ultrafast optical probes with standard surface science probes by building a novel mode-locked, regeneratively amplified femtosecond Ti:sapphire laser facility and an ultrahigh vacuum surface science chamber, and 2) to study energy transfer and surface reactions in adsorbate/substrate systems. Both of these objectives were met.

With the funds allocated under this contract we have *a)* developed a femtosecond, regeneratively-amplified Ti:Sapphire laser system, *b)* built a UHV surface science chamber, and *c)* performed novel measurements of the oxidation of CO and the desorption of O₂ on a Pt(111) surface at 90 K. See points 2-4 below for details.

2. *Ti:Sapphire Laser System:* The Ti:Sapphire regenerative amplifier produces 900- μ J pulses at a 1-kHz repetition rate. These pulses are compressed with a four-pass grating compressor to 100-fs duration, leaving 500 μ J of energy per pulse after compression. We have demonstrated that these pulses can produce a broad band continuum (from above 800 nm to below 400 nm) for use in nonlinear spectroscopy. In collaboration with ConOptics Inc. of Connecticut we studied the response of LiTaO₃ (a photorefractive material used in Pockels cells) to intense laser pulses at 800 nm to assist in development of Pockels cells in this wavelength region for commercial and military applications. Such a Pockels Cell is incorporated into our amplifier design. Using nonlinear mixing in lithium triborate (LBO) and beta-barium-borate (BBO) we produce ultrashort pulses extending into the ultraviolet (267 nm). We can produce 80–100 μ J of 400-nm second harmonic and up to 20 μ J of 266-nm third harmonic and expect to produce 1–5 μ J of 200-nm light. Pump-probe experiments are possible with a high-precision stepper motor controlled translation stage (resolution up to 0.1 μ m). We are starting construction of an optical parametric amplifier (OPA) which will be pumped with the amplified 800-nm pulses and is expected to produce 100-fs pulses with energies in excess of 50 μ J over a wavelength range from 1.1 to 2.5 μ m in the infrared.

3. *Surface Science Vacuum Chamber*: We constructed an ultrahigh vacuum (UHV) surface science chamber to prepare, maintain, and characterize atomically clean surfaces. The chamber is comprised of two levels and constructed on an optical table for maximum flexibility in optical experiments. A sample manipulator (VG Omniax) allows 4-axis positioning (as well as rotation) and motion between the two levels. The upper surface analysis/preparation level is based on a 12-inch diameter spherical shell with over 20 flanges allowing access to the sample. The lower level is a 6-inch cube with 4 custom optical quality fused silica windows permitting maximum optical access (> 90 -degree cone) for multiple laser beam optical experiments from glancing to normal incidence angles. A quadrupole mass spectrometer (UTI 100C, paid for by ARO) and a retarding field Auger/LEED (low energy electron diffraction) electron spectrometer (Omicron SpectaLEED, paid for with ARO funds) are used to characterize the surface. Translation stages allow these instruments to be positioned close to the sample for optimal sensitivity. The mass spectrometer is also used to monitor the products of laser-induced desorption. A custom designed sample heating and cooling system, using a liquid nitrogen bath and a resistive heater, makes it possible to access sample temperatures from 90 to 1250 K.

The chamber is pumped by an oil-free turbomolecular pump system (Balzers TPU 180H), an ion pump (Perkin Elmer PHI 220 L/S and controller), and a liquid nitrogen cooled cryogenic shroud (Perkin Elmer PHI TSP). During cycles of sample cleaning these primary pumps are assisted by a Titanium sublimation pump (Perkin Elmer PHI TSP and controller). A second turbopump system is used to differentially pump the rotary stage of the manipulator and to operate the gas handling systems. The base pressure of the UHV system is better than 5×10^{-11} torr.

Sample cleaning and preparation, data acquisition, and process controls are fully automated using National Instruments LabView on Macintosh computers. For sample preparation and monitoring a computer controls the sample temperature, admission of cleaning gases via programmable variable leak valves (Ne for ion bombardment, O_2 or H_2 for chemical treatment), turn on/off the sputter ion gun (Perkin Elmer), fire the Titanium sublimation pump, turn the ion gauges on or off, monitor ion pump operation, and open or close the gate valve to the turbomolecular pump. The surface preparation and characterization facilities of the UHV chamber have met or exceeded

their expectation during the CO/O₂/Pt studies.

4. We used the new equipment to study femtosecond laser induced reaction processes for O₂/Pt(111) and CO/O₂/Pt(111). We measured the O₂ desorption yield and CO₂ formation while varying the laser pulse energy (up to 300 $\mu\text{J}/\text{mm}^2$), duration (80 fs to 4 ps), wavelength (800 nm, 400-nm second harmonic, and 267-nm third harmonic), and pulse sequence (cross correlation measurements from 100 fs to 75 ps). Our experimental results, combined with numerical modeling, indicate that the laser excites electrons in the metal to temperatures in excess of 3000 K, and that these hot electrons induce desorption of O₂ in a highly nonlinear fashion. The wavelength dependence results demonstrate the importance of nonthermalized electrons under ultrashort-pulse laser irradiation conditions, calling into question the conventional assumption that the electron are thermalized before interacting with the molecules on the surface. At fluences in the range 25–120 $\mu\text{J}/\text{mm}^2$, we find that the proportion of CO₂ formation relative to O₂ desorption is reduced by more than an order of magnitude compared to cw ultraviolet irradiation. This indicates that a nonthermal reaction pathway is activated by the ultrashort laser pulses. At 266 nm, for fluences below 25 $\mu\text{J}/\text{mm}^2$, we observe a dramatic change in the branching ratio; in this regime, as in the traditional thermal regime, the CO₂ reaction product is favored over the desorption product. This is an important achievement in our pursuit of time-resolved optical studies of surface photoreactions because for the first time we have demonstrated that one can efficiently initiate a reaction with ultrashort pulses, and thereby precisely define the moment at which the reaction begins. Furthermore, the photochemical reactions used in semiconductor processing operate in this reaction dominant regime, so this result shows promise that our fundamental studies will inform understanding of real industrial processes.

These new results were accepted for publication in Chemical Physics Letters. The main findings we are reporting are: (a) the wavelength dependence we observe for the nonlinear fluence dependence cannot be accounted for by conventional theoretical models based on thermalized electron distributions; (b) we observe 2 distinct time scales in the 80-fs time-resolved cross correlation study. The 1–2-ps peak is attributed to the time scales of the electron-phonon coupling time and the

adsorbate-electron and adsorbate-phonon couplings times. The 50–100 ps response time corresponds to the cooling time of the surface to the bulk. A more detailed and in-depth paper is currently in preparation.

We also made significant progress in the description of our results. We developed a new model to describe desorption induced by electronic transfers (DIET) from nascent and thermalized electron densities (such as those created in the metal by ultrashort laser pulses). In a traditional DIET mechanism, an electron from the substrate is promoted to an adsorbed molecule, inducing that molecule to desorb. Extensions of this theory, known as DIMET, account for the nonlinear desorption arising from the hot thermalized electrons at the surface following ultra-fast laser excitation. Our model incorporates our experimental observation of a role for nascent electron distributions by allowing non Fermi-Dirac electron distributions, and explicitly including the Pt density of states. It turns out that the nascent electron distribution efficiently blocks transfer of charge from the molecule back to the substrate. The resulting bottleneck keeps the molecule in an excited state for a much longer duration than would normally be expected, leading to enhanced desorption/reaction efficiency. We plan publish the new description after carrying out additional modeling.

Our results were presented in invited and contributed talks at the following conferences: the SPIE 95 in San Diego (invited), CA; the ACS in Anaheim, CA; the CLEO/IQEC 94 in Anaheim, CA; the ACS in Washington DC, the OSA/ILS 94 in Dallas (invited); and a Gordon Conference in Ventura, CA. In addition the results were presented at invited colloquia and seminars at the following institutions: the University of California at Santa Barbara; the Center for Research and Education in Optics and Lasers at the University of Central Florida in Orlando, FL; Indiana University–Purdue University at Indianapolis; the University of Massachusetts at Lowell; and at Boston College in Newton, MA.

5. *Plan.* In the next contract period we plan to extend our work on the desorption and reaction at the Pt surface. To begin with, we will obtain more data at 266 nm and expand our studies of the wavelength dependence of the yield. We will build an optical parametric amplifier to produce tunable infrared laser pulses (1.1–2.5 μm). We

will use the infrared wavelengths to begin developing the surface coherent Raman spectroscopies required for ultrafast time resolved experiments of surface reactions. The infrared pulses will also be used to extend our studies of the wavelength dependence of the desorption and reaction processes to conditions where the ultrafast activation process is expected to be even more nonlinear. In parallel to this we will be working on the theoretical modeling of our data.

6. *ARO contacts.* The principal investigator for this project has been in regular contact with Drs. Guenther, Skatrud, and Everitt of the Army Research Office. In October 1994 Eric Mazur participated in the ARO PCOG meeting at the U.S. Military Academy at Westpoint, NY.